



PATENT SPECIFICATION

NO DRAWINGS

969,467

Date of Application and filing Complete Specification: June 11, 1963.

No. 23248/63.

Application made in Canada (No. 852,040) on June 21, 1962.

Complete Specification Published: Sept. 9, 1964.

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Index at acceptance:—C3 P(13D1A, 13F3, 13G4A, 13G4X, 13G6, 13H3, 13NX, 13R2A, 13R2B, 13T1B)

International Classification:—C 08 d

COMPLETE SPECIFICATION

Process for the production of Rubbery Polymers of Butadiene

We, POLYMER CORPORATION LIMITED, a Company organized under the laws of Canada, of Sarnia, Ontario, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the polymerization of butadiene-1,3 to produce rubbery polymer in which the monomeric units are predominantly in the cis-1,4 configuration.

In the polymerization of butadiene-1,3 the monomer units may link up in cis-1,4, trans-1,4 or 1,2 configurations. It has been established that polybutadiene may be used as a replacement for Hevea rubber. However, for this purpose, it should be predominantly in the cis-1,4 configuration.

It is known that a polymer of butadiene containing at least 75% of the units in the cis-1,4 configuration can be produced in the presence of certain stereospecific catalyst systems such as titanium tetraiodide and a Grignard reagent. These catalyst systems contain a relatively high proportion of iodine in the form of TiI_4 or molecular iodine and consequently, they are economically unattractive. The proportion of iodine can be reduced by selecting titanium iodo compounds other than titanium tetraiodide. But then, the polymer of butadiene produced in the presence of such iodo compounds of titanium and a Grignard reagent frequently is a mixture of soluble polymer and insoluble polymer. The soluble polymer is the desired rubbery polymer of a high cis-1,4 content and the insoluble is crystalline and high in trans-1,4 content. The rubbery properties of a high cis-1,4 polybutadiene are adversely affected by the presence of even a small amount of crystalline polymer.

The object of this invention is to provide a novel process for producing a rubbery polymer of butadiene in which at least 75% of the units are in the cis-1,4 configuration.

[Price 4s. 6d.]

The term "butadiene" as used throughout the specification and claims refers to butadiene-1,3 and is not intended to include butadiene-1,2 or derivatives of butadiene such as chloro-butadiene and isoprene.

The object of the invention is achieved in the process of polymerizing butadiene to produce a rubbery polymer in which at least 75% of the units are in the cis-1,4 configuration which comprises contacting butadiene with an iodine containing catalyst formed by admixing a Grignard reagent represented by the formula $RMgX$ and a titanium compound represented by the formula TiX_3Y where R is a hydrocarbon radical, X and X^1 chlorine, bromine or iodine, Y is R^1 , OR^1 , $OOCCR^1$ or an acetylacetonate radical, in which R^1 is a hydrocarbon radical containing from 1 to 18 carbon atoms, the ratio of $RMgX$ to TiX_3Y being in the range from 2:1 to 10:1, on a molar basis, and either one of the X^1 atoms or the X atom is iodine, or iodine or an iodine-releasing compound is present.

In one of its specific aspects the object of the invention is achieved in the process of polymerizing butadiene to produce a rubbery polymer in which at least 75% of the units are in the cis-1,4 configuration which comprises contacting butadiene with a catalyst formed by admixing a Grignard reagent represented by the formula $RMgI$ in which R is a hydrocarbon radical containing from 2 to 10 carbon atoms and a titanium trichloromonoalkoxide containing from 1 to 8 carbon atoms or a titanium trichloro monocarboxylate containing from 2 to 18 carbon atoms, the ratio of $RMgI$ to titanium compound being in the range from 3:1 to 7:1 on a molar basis.

The Grignard reagent which may be used in the catalyst system in the practice of the invention is a compound represented by the formula $RMgX$ where R is a hydrocarbon radical and X is a halogen atom. The term "hydrocarbon radical" includes saturated and unsaturated aliphatic radicals, cycloaliphatic radicals, and aryl, arylalkyl, alkylaryl and poly-

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cyclic aromatic radicals. The size of the hydrocarbon radical is not critical, although it is generally practical to use those having between 1 and 18 carbon at ms. The halogen atom may be selected from the group consisting of chlorine, bromine, and iodine. Representative examples of Grignard reagents which can be employed are methyl magnesium chloride, ethyl magnesium chloride, propyl magnesium chloride, allyl magnesium chloride, butyl magnesium chloride, isobutyl magnesium chloride, amyl magnesium chloride, dodecyl magnesium chloride, octodecyl magnesium chloride, cyclohexyl magnesium chloride, cyclohexenyl magnesium chloride, phenyl magnesium chloride, benzyl magnesium chloride, naphthyl magnesium chloride, and corresponding bromides and iodides. It is preferred to use a Grignard reagent in which R is a hydrocarbon radical having between 2 and 10 carbon atoms such as ethyl magnesium iodide, phenyl magnesium bromide and naphthyl magnesium chloride.

The titanium component of the catalyst system may be represented by the formula TiX_3Y in which X^1 is chlorine, bromine or iodine, Y is R^1 , OR^1 , $OOCR^1$ or an acetylacetonate radical in which R^1 is a hydrocarbon radical containing from 1 to 18 carbon atoms. The hydrocarbon radical may be an alkyl, cycloalkyl, aryl, arylalkyl or an alkyl-aryl radical. Representative examples of the titanium compounds which may be used are titanium trichloromethoxide, titanium tribromoethoxide, titanium triiodobutoxide, titanium trichloro phenoxide, titanium tribromobenzoxide, titanium triiodomonoacetate, titanium trichloromonopropionate, titanium tribromomonobenzoate, titanium triiodomonoacetylacetonate, methyl titanium trichloride, amyl titanium tribromide. Titanium iodo compounds are preferred when the Grignard reagent does not contain iodine. On the other hand, when the Grignard reagent is $RMgI$, titanium trichloro compounds such as titanium trichloro monoalkoxide are the preferred titanium compounds. When neither the Grignard reagent nor the titanium component contain an iodine atom, a third component containing iodine must be added. It may be free iodine or an iodine-releasing compound. Examples of such third components are iodine, iodine monochloride, iodine monobromide, iodine trichloride or hydrogen iodide. However, it is preferred to use a two components system containing either the iodine containing Grignard reagent $RMgI$ or a titanium iodo compound, or both.

The two components of the catalyst system may be admixed in any desired order. For example, the Grignard reagent may be added to the titanium compound or vice versa. The components may be admixed in a separate vessel and then, the mixture fed to the polymerisation reactor. Or, the components may be

added one after the other or simultaneously to the polymerization reactor and the catalyst formed in the presence of butadiene. The temperature at which the catalyst components are admixed and reacted to form the active catalyst is not critical although for best results, it should be carried out at between 0°C and 50°C.

The total amount of catalyst which is required to effect polymerization at a satisfactory rate may be readily determined by those skilled in the art. It depends on the particular conditions such as the impurities, temperature and monomer concentration. The amount usually employed varies between 0.1 and 10% by weight of the butadiene.

The relative proportions of the components of the catalyst system are also determined somewhat by the particular conditions such as temperature and the impurities present in the polymerization system, and for the production of butadiene polymers in accordance with the invention, the ratio of the Grignard reagent to the titanium compound may vary over a range from 2:1 to 10:1, on a molar basis. Higher ratios than 10:1 may also be used and will produce a high cis polymer, but they are not economical. The preferred ratio for the production of homogeneous polymers of high cis-1,4 content is between 3.0:1 and 7:1 on a molar basis.

The polymerization may be carried out over a wide range of temperatures varying from about -25°C to about 100°C. The preferred operating range is between 0°C and 50°C.

The reactants are preferably dispersed in a non-reactive liquid diluent. The liquids which are most useful for this purpose are aliphatic, cycloaliphatic and aromatic hydrocarbons such as butane, pentane, hexane, heptane, cyclohexane, benzene and toluene. Aromatic hydrocarbons containing between 6 and 8 carbon atoms are preferred for the production of polymers of the highest cis-1,4 content. However, mixtures of aromatic and aliphatic hydrocarbons can also be successfully used for producing polymers of the highest cis content.

The proportion of diluent to butadiene monomer may be varied within wide limits ranging from 0:1 to 20:1 on a weight basis. If the proportion of the diluent to the monomer is less than 1:1 on a weight basis, it is desirable that the reaction be controlled to low solids levels of not more than about 30% in order that the fluidity of the system, and the heat transfer characteristics may be satisfactory.

The invention will be described in greater detail by means of experimental results. The experiments were carried out using special grade butadiene having a purity of about 99.4%. Ethyl magnesium iodide was added as a 0.2 molar suspension finely dispersed in n-heptane. Titanium compounds were added as a 0.5 molar solution in benzene. The benzene was thiophene-free and was dried

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by azeotropic distillation. Butadiene-1,3 was dried by passing it consecutively over alumina and molecular sieves. Polymerizations were carried out in 7-oz. crown capped polymerization bottles which were thoroughly dried and flushed with nitrogen. The bottles, filled with nitrogen, were capped and the reaction components charged using a hypodermic needle inserted through a self-sealing rubber gasket.

EXAMPLE I

Butadiene was polymerized in the presence of a catalyst formed by admixing ethyl magnesium iodide and titanium trichloromonobutoxide. The ingredients were charged in the order shown in the following recipe:

Benzene	100 mls
Butadiene	20 mls
Ethyl Magnesium Iodide	variable
$\text{TiCl}_3(\text{OBu})$	0.5×10^{-3} moles

After the addition of ethyl magnesium iodide and before the addition of titanium trichloromonobutoxide, the contents of the bottles were cooled to 0°C. Polymerization proceeded for 17 hours at 25°C after which the reaction was stopped with 10 mls of ethanol. The contents of the bottles were transferred to a beaker and treated with about 100 mls of ethanol to precipitate the polymer. The polymer was next extracted with boiling ethanol to destroy and remove residual catalyst and dried under vacuum at 50°C for 16 hours. The conversion was calculated from the weight of monomer charged and the weight of polymer obtained. The structural analysis of the polymer was determined by infra-red analysis assuming that the polymer contained one double bond for each monomer unit. The results are shown in Table I.

TABLE I

Bottle No.	$\text{EtMgI}/\text{TiCl}_3(\text{OBu})$ (mole / mole)	Conversion (%)	Cis-1,4 Content (%)	1,2-Content (%)	Solubility in toluene @ 25° C. (%)
1	3	48	85.0	4.8	68
2	5	96	91.3	5.2	98
3	6.5	83	90.0	4.5	97

The polymer produced at the ratio of 3 moles of EtMgI per mole of $\text{TiCl}_3(\text{OBu})$ was a mixture of soluble and insoluble polymer. The optimum yield of homogeneous polymer of a high cis-1,4 content was obtained at the ratio of 5 moles of EtMgI per mole of $\text{TiCl}_3(\text{OBu})$.

EXAMPLE II

Butadiene was polymerized as in Example I except that 0.1 millimole of titanium trichloro monooctate was used instead of titanium trichloro monobutoxide. The molar ratio of ethyl magnesium iodide to the titanium compound was 6:1. A conversion of 10% was achieved in 60 hours at 25°C. The polymer was homogeneous and completely soluble in toluene. Analysis showed it to be made up of 85% cis-1,4 material and 8.5% 1,2 material.

WHAT WE CLAIM IS:—

1. The process of polymerizing butadiene to produce a rubbery polymer in which at least 75% of the units are in the cis-1,4 configuration which comprises contacting butadiene with an iodine-containing catalyst formed by admixing a Grignard reagent represented by the formula RMgX and a titanium compound represented by the formula TiX_3Y

where R is a hydrocarbon radical, X and X^1 are chlorine, bromine or iodine atoms, Y is R^1 , OR^1 , OOCR^1 or an acetylacetonate radical in which R^1 is a hydrocarbon radical containing from 1 to 18 carbon atoms, the ratio of RMgX to TiX_3Y being in the range from 2:1 to 10:1 on a molar basis and either one of the X^1 atoms or the X atom is iodine, or iodine or an iodine-releasing compound is present.

2. The process according to claim 1 in which R is a hydrocarbon radical containing from 2 to 10 carbon atoms.

3. The process according to claim 1 or 2 in which X is iodine.

4. The process according to claim 1, 2 or 3 in which X^1 is chlorine.

5. The process according to any of claims 1 to 4 in which Y is an alkoxide radical containing 1 to 8 carbon atoms.

6. The process according to claim 5 in which said alkoxide is butoxide.

7. The process according to any of claim 1 to 4 in which Y is a carboxylate radical containing 2 to 18 carbon atoms.

8. The process according to claim 7 in which said carboxylate radical is an octoate radical.

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9. The process according to any of the preceding claims in which the ratio of RMgX to TiX_3Y is in the range from 3:1 to 7:1, on a molar basis.
- 5 10. The process according to any of the preceding claims in which butadiene is contracted with the catalyst system at a temperature between 0°C and 50°C .
- 10 11. The process according to any of the preceding claims in which butadiene is contacted with the catalyst system in the presence of an inert hydrocarbon diluent.
- 15 12. The process according to claim 11 in which the inert diluent is an aromatic hydrocarbon.
13. The process of polymerizing butadiene to produce a rubbery polymer in which at least 75% of the units are in the cis-1,4 configuration substantially as herein described in the foregoing Examples I and II.
- 20 14. A rubbery polymer of butadiene in which at least 75% of the units are in the cis-1,4 configuration when produced by the process claimed in any of the preceding claims.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1964. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

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